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(54) **Coating composition**

(57) A water-in-oil emulsion coating composition has water dispersed in an organic solvent soluble resin and solvent through the use of an emulsifier having a hydrophile-lipophile balance of from two to six. The composition may be mixed with a hydrocarbon propellant miscible in the continuous phase in suitable containers to produce a non-foaming water containing aerosol spray paint or varnish. The composition may comprise up to 80% by weight of water. Suitable resins include vinyl toluene modified alkyd resins, oil-modified polyurethanes, acrylic resins, epoxy ester resins, aromatic hydrocarbon resins, aliphatic hydrocarbon resins and silicone resins.

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SPECIFICATION

Coating composition

This invention relates generally to coating compositions and specifically to a solvent soluble resin paint or varnish having water dispersed therein.

It has been a desideratum in the coatings art to formulate a paint, varnish or other protective coating composition which employs an organic solvent soluble film-forming component and which further includes water as part of the evaporative vehicle.

Presently such compositions, commonly called solvent or solution resin coatings, comprise organic solvents as the evaporative vehicle, often in amounts in excess of 60% of the total composition. As this solvent evaporates during the drying of the coating, considerable irritation and odor may be caused by the escape of these fumes in the atmosphere. Also, organic solvents are not inexpensive, and contribute substantially to the cost of the coating composition. In addition, as organic solvents are highly flammable they are hazardous during the manufacture and use of the coatings, and add to the fireload and insurance costs of manufacturing and warehouse facilities. For these reasons, it has been desirable to substitute water for part of the solvents previously employed.

Heretofore, water containing coatings have required water soluble or dispersable film-forming components, and latex paint, for example, has met with wide acceptance. Latex paint is composed of two dispersions. First, a dispersion of pigments and various extenders in water, and second, a dispersion of the resin in the water. The resin dispersion is either a latex formed by emulsion polymerization or a resin in emulsion form. Such paints are characterized by the fact that the film-forming component is in a water-dispersed form. The principle film-forming components in latex paints are styrene-butadiene, polyvinyl acetate, and acrylic resins.

However, latex coating compositions are not without their disadvantages. First, as the latex composition is a double dispersion, it requires two emulsifiers which may conflict and may, in particular, cause problems in formulation due to the fact that the emulsifier used in the polymerization of the resin may be unknown and have an unpredictable effect on the final product. In addition, the oil-in-water emulsion found in latex compositions will not dry to produce the clear or gloss finish found in solvent coatings such as varnish and the like. Oil-in-water emulsion clear coatings, due to the latex resins used, tend to form with brush marks or surface disruptions and cannot be easily sanded or otherwise refinished as can traditional solvent varnishes.

Also, latex coatings are not easily adaptable to use in pressurized canscommonly referred to as aerosol containers. This is due to the high viscosity of the latex composition and the tendency of the latex oil-in-water emulsion to foam excessively when sprayed from an aerosol container. This foaming begins, as the composition leaves the nozzle and becomes apparent after the coating has been applied to the substrate or workpiece. For example, previous water base spray paints dry with small craters rather than a smooth surface which indicates that foaming has occurred during the application process. Thus, when the foam dries there is left a penetrable film which seriously affects the protective film which seriously affects the protective value of the coating. In addition, as the propellant must be miscible in the continuous phase in order to properly atomize the emulsion for spraying, suitable (i.e. water soluble) propellants have led to an excessive product cost and have been otherwise unsatisfactory.

According to the present invention, a water-in-oil emulsion coating composition comprises (a) a continuous phase including a solvent; (b) a dispersed phase including water; (c) a film-forming resin dissolvable in the solvent, the continuous phase further including an effective amount of the resin for forming a film on a workpiece; and, (d) an emulsifier; the coating composition including an effective amount of the emulsifier for effecting stable dispersion of the dispersed phase throughout the continuous phase, whereupon the coating composition has as much as 80 per cent water on a weight basis, the water thereby serving to extend the solvent as to the coating composition throughout the coating composition.

The composition may be applied by brush, roller or compressed air spraying apparatus as well as being advantageously suited to being sprayed from aerosol containers such as by the inclusion of an oil-phase soluble propellant. As hereinafter described, the water-in-oil emulsion is maintained through the use of an emulsifier or an emulsifier system having a hydrophilelipophile balance, or HLB value, of from about two to about six.

Among the advantages of the present composition is that water is substituted for a large proportion of the evaporative vehicle in traditional solvent coating compositions. Thus, the invention allows the known advantages of solvent resin films to be retained in a composition having the benefits of a water based product, and a wide range of resins, including any organic solvent film-forming resin, may be used.

Substantial cost savings ar attain d becaus f the lower cost of water as compared t organic solv nts. The hazards and costs of unneeded flammable solv nts ar also mark dly reduced. Cost savings ar further realized since the traditional organic s lvent soluble resins are often less expensive than the resins heretofore used in latex oil-in-water emulsion paints. The present invention also enhances the functional utility of the paint as the resultant film may be sanded, stripped or otherwise refinished through th us of traditional methods.

The water-in-soil mulsion f the present invention may be spray d fr m aeros l c ntain rs, which are known in the art, and atomizes readily up n spraying to produce a sm th, non-foaming coating on th

workpiece to which it is applied.

The coatings referred t herein and the compositions contemplated by the present invention include those products known as varnish paint, namel, primers, lacquer and comm rcial protectiv coatings r any coating or composition wherein the film-forming resin is organic solvent soluble and which will form a water-in-oil emulsion as hereinafter described.

The percentages expressed hereinafter, both in the specification and the Claims appended thereto, relate to a preferred embodiment and are intended and expressed as percentages by weight of the total composition to which they refer.

Solvents which are contemplated by and have been found useful in the present invention include aliphatic and aromatic hydrocarbons, esters, ketones, glycol ethers and alcohols having a distillation range of from 100° to 500°F.

Although any organic solvent soluble film-forming resin is suitable for use in the present invention, resins which are preferred for use in the water-in-oil emulsion system are those with the greatest resistance to hydrolysis. Aliphatic and aromatic hydrocarbon resins possess this characteristic to a high degree, as do vinyl toluene and styrene modified resins. Epoxy ester resins also have a high resistance to hydrolysis because of the ether groups in the molecule and resultant steric hindrance found in these resins.

The water-in-oil emulsion of the present invention is adaptable to produce varnishes, wherein a clear or gloss coating is produced from the polymerization of the resin or the evaporation of the volatile portion of the vehicle. Paints such as enamels may also be produced by the addition of various organic and inorganic pigments, including carbon black, and both natural or synthetic oxides and other known colorants as hereinafter described, along with conventional pigment dispersants and anti-settling agents. Additional ingredients known in the art may also be added, such as mar resistance agents and drier catalysts.

Water is dispersed in the oil phase dependent upon the required coating composition or use, in any ratio which allows the coating to form. Emulsifiers which have been found useful in the formation of the composition of the present invention are emulsifiers having a hydrophile-lipophile balance number of from one/half to twelve.

The HLB system is a semi-empirical procedure for the selection of an appropriate emulsifier. The procedure is based on the concept that the molecule of any emulsifier contains both hydrophobic and hydrophilic groups, and the ratio of their respective weight percentages should influence emulsification behaviour.

The HLB value can be calculated from the theoretical composition of the emulsifier. For example, in determining the HLB for ethylene oxide condensation products, HLB equals one-fifth of the weight per cent of the oxyethylene hydrophilic content of the molecule. The HLB of ester emulsifiers may be calculated by the formula $HLB=20\ (1-S/A)$, wherein S is the saponification of the emulsifier and A is the acid number of the fatty acid moiety. Such methods of calculation are known in the art and expressed in a wide variety of publications.

HLB values have also been determined by titration, spreading coefficients, gas-liquid chromatograph techniques and other laboratory methods. Generally, suppliers of commercial proprietary emulsifiers provide an HLB number for their products, and published HLB indices of these materials are known in the art.

A single emulsifier having an HLB of from about two to about six may be used. However, it is preferable to use a blend of emulsifiers, including a continuous phase component as well as an emulsifier for the dispersed phase, which produce an emulsifier system having an HLB of from about two to about six. When two or more of these emulsifiers are to be blended the HLB of the combination is calculated by the formula $xA+(1-x)B$ wherein x is the per cent proportion of the emulsifier having an HLB of A and B is the HLB of the second emulsifier. It has been found that the most stable emulsion systems consist of blends of two or more emulsifiers, one portion having lipophilitic tendencies (HLB about 1/2 to about 5), and the other portion having hydrophilictendencies (HLB about 5 to about 12).

Example One

A gloss black enamel was prepared having th following comp sition:

Carbon black	1.1 %
Vinyl toluene modified alkyd resin	9.5 %
Aromatic hydrocarbon resin	5.7 %
VM & P Naphtha	15.4 %
Toluol	5.7 %
Xylol	3.2 %
Aliphatic hydrocarbon solvent boiling range, 300°-400°F.	28.4 %
Pigment dispersant (Nuosperse 657)	0.1 %
Anti-settling agent	0.1 %
Mar resistance agent	0.3 %
Drier catalyst	0.1 %
Sorbitan trioleate (Span 85, HLB 1.8)	0.32 %
Polyethylene glycol monooleate (Mapeg 200 MO, HLB 8.0)	0.08%
Water	30.0 %
	100.00%

The composition was prepared by first combining the pigment, pigment dispersant, anti-settling agent and a portion of the resin and solvent in a mixing vessel as is known in the art. The mixing was continued until the pigment was dispersed to a suitable degree of fineness. Thereafter, the remainder of the resin and solvent was added along with the mar resistance agent and drier catalyst. When the mixing was completed, the oil dispersable emulsifier, HLB 1.8, was stirred into the enamel with a homogenizer-type intensive mixer. After five minutes of mixing, a solution of water and the water dispersable emulsifier, HLB 8.0 is poured into the enamel while under constant mixing. These two emulsifiers, as hereinbefore described, yielded a total emulsifier system value of $80\% \times 1.8 + 20\% \times 8.0 = 3.04$. The water-in-oil emulsion was formed within five to ten minutes.

Example Two

In a like manner, varnish compositions may be made using the same ingredients, with the omission of the carbon black pigment and pigment related additives. Specifically, a varnish was made having the following composition:

Oil modified polyurethane resin (Urotuf 13-309)	13.9 %
Mineral spirits (boiling range 307°-389°F.)	13.9 %
Aromatic solvent (SC-100, boiling range 311°-344°F.)	31.7 %
Aromatic solvent (SC-150, boiling range 362°-410°F.)	9.4 %
Drier catalyst	0.8 %
Anti-skinning agent	0.2 %
Polyoxyethylene sorbitol beeswax derivative (Atlas G-1727, HLB 4.0)	0.2 %
Water	30.0 %
	100.0 %

SC-100 and SC-150 are known naphtha mixtures containing 98% aromatic material of C_8 or higher. Aliphatic naphthas of like boiling ranges may be used and are intended as equivalent.

Example Three

According to the same method, a gloss white enamel was prepared having the following comp sition:

Titanium dioxide	11.0 %
Vinyl toluene modified alkyd resin	14.7 %
VM & P Naphtha	14.5 %
Aliphatic hydrocarbon solvent, boiling range, 311°-344°F. (SC-100)	19.6 %
Xylol	7.5 %
Pigment dispersant (Disperse Ayd No. 1)	0.2 %
Anti-settling agent	1.8 %
Mar resistance agent	0.3 %
Drier catalyst	0.1 %
Sorbitan trioleate (Span 85, HLB 1.8)	0.25 %
Polyethylene glycol monooleate (Mapeg 200 MO, HLB 8.0)	0.05 %
Water	30.0 %
	100.0 %

The compositions described above in examples one through three were each further processed to form aerosol spray coating compositions. After the water-in-oil emulsion described above is formed, the composition was packed in an aerosol can with a suitable propellant, here propane or a mixture of propane, isobutane and/or as known in the art. The amount of propellant may vary in accordance with the intended result, but is generally in the ratio of twenty to thirty-five per cent propellant by weight in relation to the total composition. A metal or glass object weighing from five to ten grams is customarily added to the can along with the enamel. This object serves as an aid in mixing the pigment, if any, which settles to the bottom of the can during storage.

Example Four

Black Enamel using an aromatic hydrocarbon resin:

Carbon black	1.2 %
Aromatic hydrocarbon resin	19.6 %
Toluene	23.4 %
Hexane	4.9 %
Aromatic solvent, boiling range 300°-400°F.	20.0 %
Pigment dispersant (Nuosperse 657)	0.1 %
Anti-settling agent	0.2 %
Mar resistance agent	0.1 %
Drier catalyst	0.1 %
Sorbitan sesquioleate (Liposorb SQO, HLB 3.7)	0.32 %
Diethylene glycol fatty acid ester (Emcol DP-SO, HLB 5.1)	0.08 %
Water	30.00%
	100.00 %

Example Five

White Ground Marking Paint using an aromatic hydrocarbon resin:

Titanium dioxide	11.34%
Calcium carbonate	2.59%
Aromatic hydrocarbon resin	14.06%
Toluol	14.72%
Aromatic hydrocarbon solvent, boiling range 311°-344° F.(SC-100)	4.47%
Anti-settling agent	1.02%
Drier catalyst	0.22%
Pigment dispersant (Nuosperse 657)	0.34%
Sorbitan trioleate (Span 85, HLB 1.8)	0.24%
Polyethylene glycol monooleate (Mapeg 200 MO, HLB 8.0)	0.06%
Water	50.94%
	100.00%

It has been found that when water is us d in xcess f 60%, particularly when dispersed in resins having a high viscosity at high solids cont nt, a high viscosity mulsion is pr duc d due t the reduction of th effective amount of solvent for the resin and the int rnal friction created by th emulsified wat r. Thus, whil high water content may be advantageous in brushed coatings or industrial spray applications, lower viscosity emulsions should be used in the aerosol spray compositions of the present invention.

Example Six
Red Enamel using an epoxy ester resin:

Toluidine Red	1.9 %
Epoxy ester resin	14.8 %
Xylol	15.9 %
Aromatic solvent, boiling range 311°-340°F. (SC-100)	35.3 %
Pigment dispersant (Nuosperse 657)	0.06 %
Anti-settling agent	0.2 %
Mar resistance agent	0.1 %
Drier catalyst	1.0 %
Anti-skinning agent	0.3 %
Sorbitan triestearate (Liposorb TS, HLB 2.1)	0.56 %
Polyethylene glycol 200 dilaurate (Emerest 2622, HLB 6.2)	0.08 %
Water	29.8 %
	100.00 %

Example Seven
Red Fluorescent Paint using an acrylic resin:

Red Fluorescent Pigment	12.8 %
Acrylic resin	4.2 %
Aliphatic hydrocarbon solvent, boiling range 150°-200°F.	37.0 %
Xylol	15.6 %
Sorbitan trioleate (Span 85, HLB 1.8	0.35 %
Polyethylene glycol monooleate (Mapeg 200 MO,HLB 8.0)	0.09 %
Water	29.96 %
	100.00 %

Example Eight
Red Iron Oxide Primer using an Epoxy Ester:

Red Iron Oxide	5.4 %
Yellow Iron Oxide	1.6 %
Magnesium Silicate	6.8 %
Zinc Phosphate	2.6 %
Carbon Black	0.2 %
Epoxy ester resin	8.7 %
Xylol	30.4 %
Toluol	11.2 %
Anti-skinning agent	0.03 %
Pigment dispersant (Nuosperse 657)	0.15 %
Anti-settling agent	2.12 %
Drier catalysts	0.40 %
Ethylene glycol distearate (Emerest 2355, HLB 1.2)	0.34 %
Polyethylen oxide sorbitan tristearate (Liposorb TS-20, HLB 10.5)	0.09 %
Water	29.97 %
	100.00 %

Each f the compositi ns hereinb fore d scribed pr vid d a c ating comparable to the solution resin coatings as previously known at a markedly lower cost due to the inclusion of water in the composition. The

amount of water in the composition is d pendent upon the type of film desired and may vary up to 80% of th total composition.

Further, each of the compositi ns, wh n spray d fr m a standard a ros l container, resisted f aming and formed a smooth, continuous coating heretofore unobtainable in an aerosol water containing paint.

Further compositions were made including standard variations in the percentages of resin, solvent, pigments and other additives as known in the art. Oil modified polyurethane resins, epoxy ester resin, aromatic hydrocarbon resin, aliphatic hydrocarbon resin, vinyl toluene modified oil, solution vinyl resin, silicone resin and solvent soluble acrylics may be selected in accordance with the requirements of the desired application.

CLAIMS

1. A water-in-oil emulsion coating composition comprising: (a) a continuous phase including a solvent; (b) a dispersed phase including water; (c) a film-forming resin dissolvable in the solvent, the continuous phase further including an effective amount of the resin for forming a film on a workpiece; and, (d) an emulsifier; the coating composition including an effective amount of the emulsifier for effecting stable dispersion of the dispersed phase throughout the continuous phase, whereupon the coating composition has as much as 80 per cent water on a weight basis, the water thereby serving to extend the solvent as to the coating composition throughout the coating composition.

2. A coating composition as in Claim 1, wherein the emulsifier has an HLB value of from about 2 to about 6.

3. A coating composition as in Claim 1 or Claim 2, wherein the film-forming resin is selected from the group consisting of modified vinyl-toluenes, oil-modified polyurethanes, modified styrenes, epoxy glycol ethers, alcohols and mixtures thereof.

8. A coating composition as in Claim 7, wherein the continuous phase includes an effective amount of paint pigment particles for providing a desired colour, the continuous phase further including an effective amount of a pigment dispersant for effecting stable dispersion of the pigment particles throughout the continuous phase.

9. A coating composition as in Claim 8, wherein the coating composition contains from about 29 to 51 per cent water on a weight basis.

10. A method of manufacturing a water-in-oil emulsion coating composition having a continuous phase and a dispersed phase, the continuous phase including a solvent, the dispersed phase including water, and the coating composition including an effective amount of an emulsifier stable dispersion of the dispersed phase throughout the continuous phase, the method comprising: (a) adding to the solvent an effective amount of a film-forming resin thereby producing a mixture, the resin being soluble in the solvent; and (b) adding to the mixture a first effective amount of the emulsifier and to a dispersible phase a second effective amount of the emulsifier for effecting stable dispersion of the dispersible phase throughout the continuous phase and thereafter combining the dispersible phase and the mixture thereby producing the water-in-oil emulsion which is capable of forming a film on a workpiece, the emulsifier having an HLB value of from about 2 to about 6, whereupon the coating composition has as much as 80 per cent water on a weight basis, the water thereby serving to extend the solvent as to the coating composition throughout the coating composition.

11. A method as in Claim 10, wherein the film-forming resin is selected from the group consisting of modified vinyl-toluenes, oil-modified styrenes, epoxy esters, solution vinyls, silicones and mixtures thereof.

12. A method as in Claim 10, wherein the emulsifier is a system including at least two emulsifying components, a first emulsifying component having an HLB value of from about 1/2 to about 5, a second emulsifying component having an HLB value of from about 5 to about 12, the HLB value for the emulsifier system being a weighted average of the respective HLB values of the first and second emulsifying components, the method comprising adding to the mixture an effective amount of the first emulsifying component and to a dispersible phase an effective amount of the second emulsifying component for effecting stable dispersion of the dispersible phase throughout the continuous phase and thereafter combining the dispersible phase and the mixture thereby producing the water-in-oil emulsion which is capable of forming a film on a workpiece, the emulsifier system having an HLB value of from about 2 to about 6.

13. A method as in Claim 12, wherein the film-forming resin is selected from the group consisting of modified vinyl-toluenes oil-modified polyurethanes, modified styrenes, epoxy esters, solution vinyls, silicones and mixtures thereof.

14. A method as in Claim 11 or Claim 13, wherein the solvent has a distillation range of from 100 t 500 degrees Fahrenheit.

15. A meth d as in Claim 14, wherein the solvent is selected from the group consisting of esters, ketones, glycol ethers, alcohols and mixtures there f.

16. A method as in Claim 15, wherein the coating composition contains from about 29 per cent to about 51 per cent water on a weight basis.

17. A water-in-oil emulsi n coating composition substantially as hereinbefore described with reference to any one f the Examples.

18. A method of manufacturing a water-in-oil emulsion coating compositi n substantially as her inbefore described with r ference t any one of th Examples.

New claims or amendments to claims filed on 18 March 1983
New or amended claims:-

3. A coating composition as in Claim 1 or Claim 2, wherein the film-forming resin is selected from the group consisting of modified vinyl-toluenes, oil-modified polyurethanes, modified styrenes, epoxy esters, solution vinyls, silicones and mixtures thereof.

4. A coating composition as in Claims 1 and 2, wherein the emulsifier is a system including at least two emulsifying components, a first emulsifying component having an HLB value of from about 1/2 to about 5, a second emulsifying component having an HLB value of from about 5 to 12, the HLB value for the emulsifier system being a weighted average of the respective HLB values of the first and second emulsifying components and being from about 2 to about 6.

5. A coating composition as in Claim 4, wherein the film-forming resin is selected from the group consisting of modified vinyl-toluenes, oil-modified polyurethanes, modified styrenes, epoxy esters, solution vinyls, silicones and mixtures thereof.

6. A coating composition as in Claim 3 or Claim 5, wherein the solvent has a distillation range of from 100 to 500 degrees Fahrenheit.

7. A coating composition as in Claim 6, wherein the solvent is selected from the group consisting of esters, ketones,

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